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(54) **Components of catalysts for polymerizing alpha-olefins and catalysts prepared therefrom.**

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Description

This invention relates to components of catalysts for polymerizing alpha-olefins, the catalysts prepared therefrom and the use of same, in particular in the polymerization of ethylene or of mixtures thereof with alpha-olefins $CH_2{=}CHR$, in which R is an alkyl radical having 1 to 8 C for preparing crystalline copolymers and elastomeric copolymers of ethylene.

The polymerization of ethylene is carried out with co-ordination catalysts of various types, one of the most known being the reaction product of a titanium or vanadium compound with a metallorganic compound of groups I, II and III or the periodic system.

As is known, the use of vanadium catalysts permits to obtain, differently from the Ti catalysts, polyethylene with a rather wide molecular weight distribution (MWD).

From patent FR 2 378 047 components of catalysts for polymerizing ethylene are known, which are prepared by reacting vanadium halogenated compounds having a valence higher than 3 (for example VCl_4, $VOCl_3$) with an aluminium alkyl in the presence of an ether.

The reaction product comprises or essentially consists of VCl_3.

The catalysts obtained from said catalyst components by reaction with an aluminium alkyl have a rather high activity, although not so high as to lead to the forming of polymers having a low content of catalyst residues, in particular having residual V contents lower than a few ppm.

In fact it is known that polymers containing V in amounts higher than a few ppm are physiologically prejudicial, heretofore the polymers obtained with said catalyst had to be sujected to long and expensive purification processes.

In the field of elastomeric copolymers the polymerization of ethylene and of alpha-olefins in the presence or in the absence of diolefins has been effected till now with catalysts of different types: one of the most used is composed of the reaction product of a vanadium compound and by a metallorganic compound of the metals of groups I, II and III of the Periodic System.

Said copolymerization is preferably effected by using catalysts which are soluble and highly dispersible in the polymerization medium such as: vanadium halides and oxyhalides, alocoholates and acetylacetonates of vanadium and of vanadyl.

By using these cataylsts it is possible to obtain substantially amorphous copolymers, characterized, in the vulcanized state, by valuable elastomeric properties. The polymer yields referred to the catalyst employed, however, are not so high as to lead to the forming of polymers having a low content of catalyst residues, in particular having a low content of residual vanadium.

Attemps have been made to obviate this disadvantage by employing activating substances, but also in such case the yields remain always very low and do not permit to avoid purifying the polymer from the catalyst residues.

Therefore the need was felt of having available V catalysts having a high activity and enabling to obtain ethylene polymers containing such percentages of V as to avoid any purification of the polymer, and simultaneously enabling to obtain a polymer with a broad MWD.

From CA-A 716 176 a catalyst for polymerizing olefins is known obtained by reacting the complex $VCl_3 \cdot C_2H_5OH$ with $Al(C_2H_5)_2Cl$.

It is an object of the present invention to prepare catalysts components based on V for polymerizing olefins, particularly suited to polymerize enthylene or mixtures thereof with alpha-olefins $CH_2{=}CHR$, in which R is an alkyl radical having 1-8 C or of said alpha-olefins with one another, such catalyst components permitting to obtain crystalline copolymers containing a very low vanadium percentage, so that they may be physiologically harmless and one can obtain saturated elastomeric copolymers of ethylene and unsaturated elastomeric copolymers where there is also used a hydrocarbon monomer containing more than one double bond, when employed in admixture with aluminium alkyls.

It has been now surprisingly found that chlorinated compounds of trivalent vanadium having certain X-ray powder spectrum and obtained according to the process specified below can be advantageously used as components of catalysts for the polymerization of olefins said above and in particular of ethylene or of mixture thereof with alpha-olefins containing, in case, hydrocarbon monomers with more than one double bond.

By reaction with an Al metallorganic compound said components form catalysts which are very active in the polymerization of olefins as stated above.

The polymer obtained contains such amounts of catalyst residues as not to require, generally, any purification process.

Accordingly the invention is directed to a process for preparing a catalyst component (component a) for polymerizing olefins, comprising a chlorinated compound of trivalent vanadium of general formula

$$VCl_n(OR)_m$$

wherein

R = a hydrocarbon radical having 1 to 18 carbon atoms, in particular an alkyl with 1 to 10 carbon atoms, a cycloalkyl with 6 to 8 carbon atoms, or an aryl or a radical $R^1_pSi(OH)_{3-p}$ in which R^1 is a hydrocarbon radical having the same meaning as R and $1 \leqslant p \leqslant 3$, n = a number from 1.5 to 3, m = 3-n; with X-ray powder spectrum, in which the maximum intensity diffraction lines, which in the spectrum of normal VCl_3 appear at $d = 5.75 \cdot 10^{-10}$ m, $d = 2.67 \cdot 10^{-10}$ m and $d = 1.74 \cdot 10^{-10}$ m, exhibit a broadening of the half peak breadth of at least three times for the diffraction line at $d = 5.75 \cdot 10^{-10}$ m and of at least four times for the diffraction line appearing at $d = 2.67 \cdot 10^{-10}$ m and d

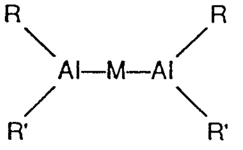
$= 1.74 \cdot 10^{-10}$ m, or said diffraction lines disappear, in which a chlorinated compound of trivalent vanadium is reacted with an organic compound, containing at least one -OH group and the resulting reaction product is decomposed at 30° to 200°C with a halogenated substance capable of reacting with the -OH group present in the reaction product, selected from the group consisting of tetrahalides of Sn or Si, $Cl_2Si(CH_3)_2$, Cl_3SiCH_3, $SbCl_3$, $AlCl_3$, $TiCl_4$ and $VOCl_3$.

In the above formula m + n may be slightly different from 3 in view of the possible analytical errors.

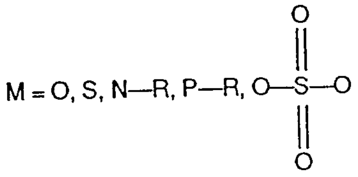
By the expression 'normal vanadium chloride' we mean VCl_3 having a spectrum, on X-ray analysis, reported in ASTM 15-382.

The invention is further directed to a catalyst component for polymerizing olefins obtained according to the above stated process.

Another object of this invention is a catalyst for polymerizing ethylene or mixtures thereof with alpha-olefins $CH_2{=}CHR$, in which R is an alkyl radical having 1-8 C, containing, in case, hydrocarbon monomers with more than one double bond, obtained by reacting catalyst component a) with b), a metallorganic compound of Al, preferably Al-trialkyl compound or a compound of Al or general formula:



wherein:



M = O, S, N—R, P—R, $O{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}{-}O$

and R may be a hydrocarbon radical with 1-20 C, in particular an alkyl having 1-18 C, an aryl, and R′ may be R or a halogen or an alkoxyl.

Some vanadium compounds representative of the catalytic component are:

$VCl_2(OC_4H_9)$, $VCl_{1.5}(OC_4H_9)_{1.5}$, VCl_3, $VCl_{2.8}(OC_2H_5)_{0.2}$, $VCl_2(OC_6H_5)$, $VCl_2(OC_8H_{17})$, $VCl_2[OSi(CH_3)_3]$, $VCl_{1.5}[OSi(CH_3)_3]_{1.5}$.

In the process for preparing the catalyst component a) the reaction between the chlorinated compound of trivalent V and the organic compound containing at least one -OH group can occur either in the presence or in the absence of solvents at temperatures ranging from 0°C to the boiling temperature of the organic compound containing at least one -OH group, employing the organic compound containing at least one group -OH in molar excess and appropriately molar ratios between the V compound and the organic compound containing at least one -OH group comprised between 2 and 300.

The utilizable organic compounds containing at least one group -OH are selected between alcohols and thioalcohols, phenols and thiophenols having 6 to 18 carbon atoms and the silanols $R^{1}_{p}Si(OH)_{4-p}$, in which R′ has the meaning already specified and $1 \leqslant p \leqslant 3$.

Useful alcohols are for example: aliphatic alcohols, cycloaliphatic alcohols, aromatic alcohols, containing 1 to 18 C.

Employable aliphatic alcohols are for example: methyl, ethyl, propyl, butyl, hexyl, octyl alcohols.

Cycloaliphatic alcohols which can be used are: cyclopentanol, cyclohexanol.

Examples of aromatic alcohols are: benzyl alcohol, alpha-phenyl ethyl alcohol.

As phenol it is possible to employ: phenol, cresol and substituted phenols.

Examples of silanols are trimethylsilanol, triphenylsilanol, butyltrisilanol.

The preferred starting V compound is VCl_3.

The decomposition of the product obtained from the reaction between the trivalent V compound and the organic compound containing at least one group -OH can be effected with the above mentioned halogenated compounds, optionally in the presence of a solvent, using a molar excess of the halogenated compound. The preferred halogenated compounds are $SnCl_4$, $SiCl_4$ and $Ticl_4$. There are provided compounds which are soluble in the reaction medium.

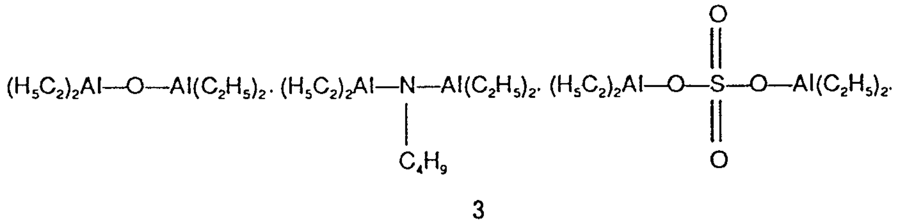
If $SiCl_4$ is utilized as an agent for decomposing the product of the reaction between the trivalent V compound and the organic compound containing at least one -OH group, a small amount of Si compound, from 0.5 to 7% by weight as Si, may remain in the product. When for the decomposition $TiCl_4$ is employed as halogenated compound, a product is obtained, in which the OR groups are practically absent and the Ti amount ranges from 0.5 to 10% by weight is contained.

Representative examples of the Al metallorganic compounds to be employed as components b) of the catalysts are the following:

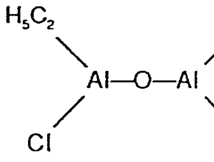
$Al(C_2H_5)_3$, $Al(i{-}C_4H_9)_3$, $Al(I_2H_5)_2Cl$, $Al(n{-}C_3H_7)_2Cl$, $Al(i{-}C_4H_9)_2H$, $Al(C_8H_{17})_3$, $Al(C_8H_{13})_3$.

It is preferable, however, to use Al metallorganic compounds containing two or more Al atoms bound to one another heteroatoms.

Typical examples of such compounds are:



$$(H_5C_2)_2Al{-}O{-}Al(C_2H_5)_2,\ (H_5C_2)_2Al{-}\underset{\underset{\displaystyle C_4H_9}{|}}{N}{-}Al(C_2H_5)_2,\ (H_5C_2)_2Al{-}O{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}{-}O{-}Al(C_2H_5)_2.$$



, $(i\text{-}C_4H_9)_2Al—O—Al(i\text{-}C_4H_9)_2$.

How to prepare these compounds is known from the literature.

The ratio between component b) and component a) is higher than 1 and is generally comprised in a wide range, ratios between 5 and 500 being preferably employed.

In case the catalysts are employed to polymerize propylene to form a polymer highly isotactic, it is necessary to modify both component a) and component b) with an electron-donor compound as already described in the literature for supported catalysts containing titanium, for example in GB patent No 1 559 194.

As a further improvement of the present invention, it has been found that if component a), obtained by decomposition of the reaction product between the starting V compound and the organic compound containing -OH groups with halogenated compounds different from Ti halogenated compounds, is treated with a liquid halogenated Ti compound under the reaction conditions, catalysts are obtained, which provide very high yields without effecting the MWD.

Examples of Ti compounds to be used are the tetravalent Ti halogenated compounds, such as $TiCl_4$, $TiBr_4$ and Ti halogen-alcoholates.

The reaction with the Ti compound is preferably conducted in an excess of the liquid Ti compound with successive separation of the unreacted compound. If $TiCl_4$ is utilized as reagent and as reaction medium, the reaction temperature generally ranges from 50°C to the $TiCl_4$ boiling point, in particular from 80° to 135°C.

The catalyst component of this invention can be supported, according to known techniques, on carriers such as silica, alumina, Mg halides in the activated form, as is described for example in GB patent 1 292 853, or diluted inert solid substances.

The catalysts according to the present invention are employed in the polymerization of ethylene, or of alpha-olefins $CH_2=CHR$ in which R is an alkyl radical having from 1 to 8 C atoms, or for copolymerizing ethylene with said alpha-olefins, for preparing crystalline polymers and copolymers of ethylene or of said alpha-olefins.

The (co)polymerization is conducted according to known techniques, operating in a liquid phase, either in the presence or not of an inert hydrocarbon diluent, such as hexane, heptane, cyclohexane etc., or in the gas phase.

The (co)polymerization of ethylene is generally carried out at a temperature less than 150°C, and at pressures less than $50.7 \cdot 10^5$Pa, or at temperatures ranging from 150°C and 300°C and at pressures higher than $10.1 \cdot 10^5$Pa.

The polymerization of alpha-olefins, is generally carried out at temperatures ranging from 50°C to 150°C, preferably between 40°C and 90°C, and at atmospheric pressure or at a higher pressure.

The ethylene polymers obtained have densities higher than 0.95 g/cm³, the crystalline copolymers of ethylene contain up to about 10% by moles of alpha-olefins and have densities ranging from 0.91 to 0.95 g/cm³; said (co)polymers are endowed with good mechanical properties and in particular have a broad distribution of molecular weight (MWD). The ratio MWD between $M\bar{w}$, weight average of molecular weight, and $M\bar{n}$, number-average molecular weight, is higher than 10.

The catalysts according to the present invention can also be employed in the copolymerization of ethylene with an alpha-olefin selected from propylene, butene-1,4-methyl-pentene-1, in the presence or not of a hydrocarbon monomer as third monomer containing more than one double bond, for preparing elastomeric copolymers according to known techniques.

As hydrocarbon monomer containing more than one double bond can be used dienes and polyenes. As dienes can be used for example butadiene-1,3, isoprene, hexadiene-1,4, dicyclopentadiene, decatriene-1,4,9, 4-vinylcyclohexene, cyclooctadiene-1-5.

The ethylene content in the binary saturated elastomeric copolymers generally range from 20% to 80% by weight. The third monomer content in the unsaturated elastomeric copolymers ranges from 0.1 to 20% by moles.

The following examples are given merely for illustrating the present invention, withtout bringing, however, a limitation thereof.

Preparation of catalyst component a)

Examples 1-7

Various catalytic components of the catalyst both for the polymerization of ethylene and for the copolymerization of ethylene with alpha-olefins were prepared by operating as follows.

4.07 g of anhydrous VCl_3 in powder were dissolved, in a glass vessel equipped with a magnetic stirrer, in a N_2 atmosphere, in 50 ml of anhydrous alcohol.

The resulting solution was evaporated to dryness till obtaining a solid product.

The solid product so obtained was decomposed with 200 ml of $SiCl_4$ and it was maintained at reflux for 48 hours.

In example 5, an equimolecular amount of Cl_2SiCH_4 instand of $SiCl_4$ was used as decomposing agent of the reaction product between VCl_3 and alcohol.

In examples 6 and 7, an equimolecular amount of $TiCl_4$ (double treatment at 130°C for 2 hours) was used instead of $SiCl_4$.

The resulting violet solid was isolated by filtration, it was repeatedly washed with portions of 500 cc each of anhydrous n-heptane, finally it was dried under vacuum (at $0.67 \cdot 10^2$ Pa) for at least 1 hour at 20°C.

In all the examples the final product obtained was essentially a violet solid compound in powder having general formula $VCl_n(OR)_m$, wherein n and m vary from 1.5 to 3, the extremes being included, and contained variable amounts of Si or Ti, depending on the reagents used.

The spectra, on X-ray analysis, of the products of examples 6, 7 exhibited a broadening of the half peak breadth of the lines of maximum intensity which in the powder spectrum of normal VCl_3 appear at: $d = 5.75 \cdot 10^{-10}$ m, $d = 2.67 \cdot 10^{-10}$ m and $d = 1.74 \cdot 10^{-10}$ m.

The spectra, on X-ray analysis, of the products of examples 1 to 5 were characterized in that they did not show the lines of maximum intensity which in the spectrum of normal VCl_3 appear at the above-mentioned values.

Example 8

5.3 g of the catalyst component prepared as in examples 1 to 5 were treated with 100 ml of $TiCl_4$ at 130°C for 2 hours, $TiCl_4$ was removed by filtering at 130°C and an equal amount thereof was added, it was allowed to react at the same temperature for 2 hours, whereupon it was filtered at 130°C to remove $TiCl_4$ and it was washed at 90°C with n-heptane until disappearance of the chlorine ions in the filtrate.

The elementary analysis of the solid product dried under vacuum is reported on Table I.

The spectrum, on X-ray analysis, is of the type of examples 6–7.

Table I
Preparation of catalyst component a)
$VCl_n(OR)_m$

Example No.	ROH	Analysis of the component			
		V (% by weight)	Cl (% by weight)	OR (% by weight)	Ti (% by weight)
1	C_2H_5OH	23.75	43.3	13.0	—
2	CH_3OH	26.7	46.2	5.42	—
3	C_4H_9OH	25.2	42.0	29.2	—
4	$C_8H_{17}OH$	22.4	37.1	28.6	—
5	C_2H_5OH	25.44	41.7	14.94	—
6	C_2H_5OH	18.1	58.8	—	9.62
7	C_4H_9OH	22.0	59.6	—	8.9
8	C_2H_5OH	15.95	50.3	—	5.56

Example 9

3.5 g of anhydrous $MgCl_2$ in powder and 8.1 g of anhydrous VCl_3 in powder were dissolved in 150 ml of anhydrous C_2H_5OH at room temperature in a vessel equipped with a magnetic stirrer. The resulting solution was evaporated to dryness until obtainment of a green solid product. The solid product so obtained was treated with 200 ml of $TiCl_4$. The temperature was then brought to 110°C and maintained at such level for 2 hours.

The resulting violet solid was isolated by filtration and it was treated again with 400 cc of $TiCl_4$ for 2 hours at a temperature of 135°C. It was washed with n-heptane until disappearance of the chlorine ions in the filtrate.

The elementary analysis of the dried solid is reported on Table II.

Example 10

Example 9 was repeated using 7.8 g of VCl_3, 3.4 g of $MgCl_2$ and 100 ml of C_2H_5OH respectively.

The solid product obtained by means of the process according to example 9 was treated at reflux with 200 ml of $SiCl_4$ for 48 hours. It was filtered and the resulting solid product was repeatedly washed with n-heptane.

The elementary analysis of the solid obtained is reported on Table II.

Table II

Example No.	Analysis of the component				
	V (% by weight)	Cl (% by weight)	Ti (% by weight)	Si (% by weight)	Mg (% by weight)
9	15	54.2	7.2	—	5.2
10	15.7	45.5	—	7.9	4.0

Polymerization of ethylene

Examples 11–32

The catalyst components prepared in examples 1 to 10 mixed with Al-alkyls formed the catalysts which were utilized in the polymerization of ethylene.

Polymerization was carried out under the following conditions:

100 ml of anhydrous desulphurized and deaerated n-heptane, component b) as co-catalyst and finally a proper amount of component a) were introduced in the order into a 3-liter autoclave equipped with an anchor stirrer and heated at the desired temperature. Hydrogen and ethylene at the prefixed partial pressures were added and the total pressure was kept constant for the duration of polymerization by continuously feeding ethylene.

Polymerization was stopped after a proper reaction period, the suspension was discharged from the autoclave, it was filtered and the polyethylene was dried in an oven to constant weight.

The amounts of the components used, conditions and temperature at which polymerization was conducted and the physical properties of the polymer obtained are recorded on Table III.

The polymer melt index was measured according to standards ASTM D 1238 (conditions E and F) and is expressed in g/10 min.

Table III

Example No.	Catalyst component	Co-catalyst		Polymerization conditions				Polymer				
	Example No.	aluminium alkyl	conc. (mm/l)	T (°C)	pH_2 (.10^5 Pa)	pC_2H_4 (.10^5 Pa)	t (h)	yield (Kg PE/g cat.)	η Inh (dl/g)	Melt Index (g/10′)		$M_{\bar{w}}$ / $M_{\bar{n}}$
										MI E	MI F	
11	1	$Al(IC_4H_9)_3$	1	85	1	12.2	4	17	1.61	1.39	81	10.96
12	1	$Al(IC_4H_9)_3$	1	70	1.5	11.7	4	15	2.02	0.47	36.9	11.42
13	1	$Al(nC_6H_{13})_3$	1	70	1.5	11.7	4	13	1.99	0.41	60.4	16.52
14	1	$(C_2H_5)_2AlOCH_3$	2.5	70	2	11.2	4	15.3	1.67	1.8	122.2	22.32
15	1	$(C_2H_5)_2AlOCH_3$	2.5	85	1	12.2	4	18.2	1.73	1.6	86.9	13.4
16	1	$[(IC_4H_9)_2Al]_2O$	4	85	1	12.2	2	47.5	2.25	0.34	24.6	13.94
17	1	$[(IC_4H_9)_2Al]_2O$	4	75	2	11.2	2	30	1.43	2.17	156	21.38
18	1	$[(nC_6H_{13})_2Al]_2O$	4	75	2	11.2	2	22	1.52	2.8	166	16.35
19	2	$[(IC_4H_9)_2Al]_2O$	4	85	1.5	11.7	2	24	2.66	0.14	12.3	20.12
20	3	$Al(IC_4H_9)_3$	1	85	1	12.2	4	12.8	2.12	0.44	26.4	15.03
21	3	$[(IC_4H_9)_2Al]_2O$	4	85	1	12.2	4	36	2.96	0.043	4	15.41
22	4	$[(IC_4H_9)_2Al]_2O$	4	85	1.5	11.7	2	41	2.44	0.25	15.3	12.66
23	5	$Al(IC_4H_9)_3$	1	85	1	12.2	4	16	2.03	0.41	31.3	12.01
24	1	$[(IC_4H_9)_2Al]_2NC_4H_9$	4	85	1.5	11.7	2	26.7	2.06	0.47	33.3	12.46
25	1	$[(C_2H_5)_2Al_2]SO_4$	4	85	1.5	11.7	2	52.4	1.94	0.64	42.1	21.01
26	8	$[(C_4H_9)_2Al]_2O$	4	85	6.1	8.1	2	42.7	2.15	0.54	20.7	12.1
27	8	$[Al(IC_4H_9)_3]$	4	85	6.1	8.1	2	33.4	2.30	0.26	13	16.3
28	8	$[Al(C_6H_{13})_3]$	1.5	70	8.1	6.1	4	12.5	3.29	0.1	6.23	19.53
29	6	$Al(C_6H_{13})_3$	1.5	85	7.1	7.1	1	50	1.95	0.58	37.2	18.66
30	7	$Al(IC_4H_9)_3$	5	70	7.1	7.1	2	23.6	2.86	0.04	6.40	14.67
31	9	$Al(IC_4H_9)_3$	5	70	7.1	7.1	1	18.8	2.08	0.5	28.7	11.59
32	10	$Al(C_6H_{13})_3$	3	70	7.1	7.1	3	29.4	1.98	0.76	28.7	23.31

Copolymerization of ethylene

Examples 33–35

The catalyst components prepared in examples 1 to 10 mixed with Al-alkyls formed the catalysts which were employed in the copolymerization of ethylene with minor amounts of alpha-olefins for obtaining crystalline copolymers of ethylene.

Copolymerization was carried out under the following conditions:

a 3-liter autoclave equipped with an anchor stirrer and heated at the desired temperature was fed in the order with: 480 ml of anhydrous desulphurized deaerated n-heptane, 4 m moles of $(iC_4H_9)_2Al\text{-}O\text{-}Al(iC_4H_9)_2$ as co-catalyst, a suitable amount of butene-1, the desired amount of H_2, and ethylene up to a total pressure of $14.2 \cdot 10^5$ Pa. After 5 minutes 10 mg of the solid catalytic component a) described in example 1 suspended in 20 ml of n-heptane were introduced under an argon overpressure, the total pressure having been maintained constant by continuously feeding ethylene. After 10 minutes the test was stopped and the polymer was isolated after having removed the unreacted monomers.

The amount of butene-1, the polymerization conditions and the physical characteristics of the copolymers obtained are reported on Table IV.

Table IV
Copolymerization of ethylene

		Polymerization conditions			Polymer			
Example No.	Butene-1 (g)	T (°C)	pH_2 ($.10^5$ Pa)	polymer g	C_4 (% b.w.)	d (g/cm³)	melt point (°C)	η inh. (dl/g)
33	20	70	1	90	3.5	0.946	126	1.29
34	40	70	0.5	105	5.1	0.925	122.5	2.15
35	20	85	0.5	122	3.7	0.938	124.5	2.03

Example 36

A 1.5-liter autoclave equipped with an anchor stirrer and at room temperature was fed in the order with:

0.7 g of $[(iC_4H_9)_2Al]_2O$ in n-heptane solution containing 134 g/l, and 415 g of butene-1.

It was heated at the temperature of 65°C (butene-1 pressure = $7.6 \cdot 10^5$ Pa) and was added hydrogen up to a pressure of $9.7 \cdot 10^5$ Pa and then ethylene up to a pressure of $36.5 \cdot 10^5$ Pa. 7.7 mg of the catalyst component obtained according to the example 1 in 20 cc of n-pentane were then introduced by means of a steel syringe under an ethylene overpressure.

Ethylene was added up to a pressure of $39.6 \cdot 10^5$ Pa (ethylene pressure = $29.9 \cdot 10^5$ Pa).

During the test the pressure was kept constant by feeding ethylene.

The test was stopped after 2 hours and after having removed the unreacted monomers, the polymer was isolated and dried in an oven at 70°C to constant weight.

The amount of polymer was 220 g.

The yield was of 120,000 g/g of V (28,600 g/g of catalyst).

The copolymer showed at infrared spectrographic analysis a butene content of 10.5% by weight. The density was of 0.9166 g/cm³, ηinh of 1.6 dl/g, $M.I._E = 1.75$ g/10′ and $M.I._F = 180$ g/10′.

Elastomeric copolymers of ethylene

Example 37

22 mg of the catalyst component obtained, according the example 1, mixed with 1 cc of $Al(iC_4H_9)_3$ in 20 cc of n-heptane, constituted the catalyst for the polymerization.

500 g of propylene were introduced, at room temperature, into an autoclave having a capacity of 3,000 cm³, equipped with an anchor stirrer; the temperature was brought to 40°C (propylene pressure $16.2 \cdot 10^5$ Pa) and ethylene was added up to a pressure of $22.3 \cdot 10^5$ Pa.

The catalyst was then introduced by means of a steel syringe under an argon overpressure. During the test the pressure was kept constant by feeding ethylene. The test was stopped after 4 hours. The amount of polymer dried under vacuum was of 150 g.

The yield was of 28,000 g/g of V (6,800 g/g of catalyst).

The copolymer, subjected to infrared spectrographic analysis, showed a propylene content of 39% by weight.

On X-ray analysis the copolymer exhibited a crystallinity of the polyethylene type of 2% by weight.

Example 38

500 g of propylene were introduced, at room temperature, into the autoclave described in example 37.

The temperature was brought to 40°C (propylene pressure = $16.2 \cdot 10^5$ Pa) and ethylene was introduced up to a total pressure of 22 atm. Successively, 21 mg of the catalyst component prepared according to example 37, mixed with 8 cc of a 0.5 M solution of $(iC_4H_9)_2Al\text{-}O\text{-}Al(iC_4H_9)_2$ in 20 cc of n-heptane, were introduced by means of a steel syringe under an argon overpressure.

During the test the pressure was maintained constant by feeding ethylene. Polymerization was stopped after 4 hours. The polymer dried under vacuum amounted to 160 g. The yield was of 31,000 g/g of V (7,600 g/g of catalyst).

Under infrared spectrographic analysis the copolymer revealed a propylene content of 45% by weight. Under X-rays analysis the copolymer exhibited the presence of crystallinity of the polyethylene type of 3% by weight.

Propylene polymerization

Example 39

8 g of anhydrous VCl_3 in powder were dissolved in 100 ml of anhydrous C_2H_5OH in the vessel described above. The resulting solution was evaporated till obtaining a solid product.

7.81 g of the solid product so obtained were added to 200 ml of $SiCl_4$ and 8.8 m moles of ethyl benzoate (EB) in heptane solution. It was maintained at reflux for 48 hours and then the resulting solid was isolated by filtration, washed with portions of 50 cc each of anhydrous n-heptane and dried under vacuum for 1 hour at 20°C.

4.77 g of the solid product so obtained was treated with 200 ml of $TiCl_4$ and heptane solution containing 2.2 m moles of EB. It was heated to 120°C and kept at such temperature for two hours. It was filtered and an equal amount of $TiCl_4$ was added again, it was allowed to react at the same temperature for two hours, where upon it was filtered to remove $TiCl_4$ and washed at 90°C with n-heptane until disappearance of chlorine ions in the filtrate. The solid dried under vacuum exhibited on analysis the following contents by weights:

Ti = 4.4%, V = 24.2%, Cl = 59.9%, EB = 1.57%.

Propylene polymerization was carried out under the following conditions:

3.75 m moles of an aluminium trialkyls mixture, having the following composition of the gases (% by volume) after hydrolysis:

ethane = 9
isobutane = 49.4
n-butane = 41.2
propane = 0.16
isobutane = 0.24

were reacted at room temperature with 1.13 m moles of methylparatoluate in 80 ml of n-heptane (anhydrous and desulphurized) for 5 minutes.

50 ml of such solution were contacted with a 120 mg of the catalyst component prepared above.

The remaining 30 ml were diluted to 1,000 ml with n-heptane and introduced, under a nitrogen pressure, into a steel autoclave, having a capacity of 3,000 ml, equipped with anchor magnetic stirrer and thermometer, thermoregulated at 40°C, whereinto propylene was made to flow.

In the same way, the catalytic component suspension was then introduced thereinto. After closing of the autoclave, hydrogen was added up to a partial pressure of $0.1 \cdot 10^5$ Pa, then it was heated to 70°C under simultaneous feeding of propylene up to a total pressure of $7.1 \cdot 10^5$ Pa; then it was heated to 70°C under simultaneous feeding of propylene up to a total pressure of $7.1 \cdot 10^5$ Pa. Such pressure was kept constant throughout the polymerization by going on feeding the monomer.

After 4 hours polymerization was stopped and polypropylene was isolated by treatment with methanol and acetone.

The results of the polymerization were: yield = 2.33 kg of polymer/g of catalyst, heptane residue to the extraction with boiling n-heptane was 91.3, ηinh = 3.87.

Claims

1. A process for preparing a catalyst component for polymerizing olefins, comprising a chlorinated compound of trivalent vanadium of general formula

$$VCl_n(OR)_m$$

wherein

R = a hydrocarbon radical having 1 to 18 carbon atoms, in particular an alkyl with 1 to 10 carbon atoms, a cycloalkyl with 6 to 8 carbon atoms, or an aryl or a radical $R^1_pSi(OH)_{3-p}$ in which R^1 is a hydrocarbon radical having the same meaning as R and $1 \leqslant p \leqslant 3$, n = a number from 1.5 to 3, m = 3-n;

with X-ray powder spectrum, in which the maximum intensity diffraction lines, which in the spectrum of normal VCl_3 appear at $d = 5.75 \cdot 10^{-10}$ m, $d = 2.67 \cdot 10^{-10}$ m and $d = 1.74 \cdot 10^{-10}$ m, exhibit a broadening of the half peak breadth of at least three times for the diffraction line at $d = 5.75 \cdot 10^{-10}$ m and of at least four times for the diffraction line appearing at $d = 2.67 \cdot 10^{-10}$m and $d = 1.74 \cdot 10^{-10}$ m, or said diffraction lines disappear, in which a chlorinated compound of trivalent vanadium is reacted with an organic compound, containing at least one -OH group and the resulting reaction product is decomposed at 30° to 200°C with a halogenated substance capable of reacting with the -OH group present in the reaction product, selected from the group consisting of tetrahalides of Sn or Si, $Cl_2Si(CH_3)_2$, Cl_3SiCH_3, $SbCl_3$, $AlCl_3$, $TiCl_4$ and $VOCl_3$.

2. A process according to the preceding claim in which VCl_3 is used as V compound, C_2H_5OH as organic compound containing -OH groups, and the decomposition is effected with $SiCl_4$.

3. Catalyst component for polymerizing olefins obtained according to the process of claims 1 and 2.

4. Catalyst component for polymerizing olefins formed of a component according to claim 3 obtained by decomposition of the reaction product between the starting chlorinated V compound and the organic compound containing -OH groups with halogenated compounds different from Ti halogenated compounds, and a liquid Ti halogenated compound.

5. The catalyst component according to claim 4, in which the Ti halogenated compound is $TiCl_4$.

6. The catalyst component of the preceding claims supported on $MgCl_2$.

7. Catalyst for (co)polymerizing olefins comprising the product of the reaction of:

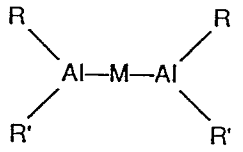
a) a halogenated compound of V as obtained according to the process in claims 1 and 2 with

b) a metallorganic compound of Al.

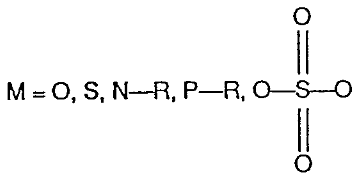
8. A catalyst according to claim 7 in which in the formula of the catalyst component a) n = 2, m = 1 and R is a hydrocarbon radical C_4H_9.

9. A catalyst according to claim 7 and 8 in which the component a) has the formula $VCl_2(OC_2H_5)$.

10. The catalyst according to claim 7 in which component b) is a metallorganic compound of Al selected from the Al-trialkyls and compounds having the general formula:



wherein:



$M = O, S, N{-}R, P{-}R, O{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}{-}O$

R may be a hydrocarbon radical with 1-20 C, in particular an alkyl having 1-18 C,

R′ is equal to R or is a halogen or an alkoxyl.

11. The catalyst according to claims 7 and 10, in which M = O.

12. The catalyst according to the preceding claims 7 to 11 comprising the product of the reaction of:

a) $VCl_2(OC_2H_5)$ with

b) $(iC_4H_9)_2$-Al-O-Al-$(iC_4H_9)_2$

13. A process for the polymerization of ethylene, or for copolymerizing ethylene with alpha-olefins $CH_2{=}CHR$ in which R is an alkyl radical having from 1 to 8 C atoms, for preparing crystalline polymers and elastic copolymers of ethylene, characterized in that polymerization is carried out in the presence of the catalysts according to claims 7 to 12.

14. A process for the copolymerization of ethylene with an alpha-olefin selected from propylene, butene-1, 4-methyl-pentene-1, for preparing elastomeric saturated copolymers of ethylene, characterized in that monomers are polymerized in the presence of the catalyst according to claims 7 to 12.

15. A process according to claim 14 characterized in that the copolymerization is carried out in the presence of a third monomer containing more than one double bond selected from dienes and polyenes.

Patentansprüche

1. Verfahren zur Herstellung einer Katalysatorkomponente zur Polymerisation von Olefinen, enthaltend eine chlorierte Verbindung des dreiwertigen Vanadins der allgemeinen Formel

$$VCl_n(OR)_m$$

worin

R = ein Kohlenwasserstoffrest mit 1 bis 18 Kohlenstoffatomen, insbesondere ein Alkylrest mit 1 bis 10 Kohlenstoffatomen, eine Cycloalkylgruppe mit 6 bis 8 Kohlenstoffatomen oder eine Arylgruppe oder ein Rest $R^1_pSi(OH)_{3-p}$, worin R^1 für einen Kohlenwasserstoffrest mit der gleichen Bedeutung wie R steht und $1 \geqslant p \geqslant 3$, n = eine Zahl von 1,5 bis 3, m = 3-n;

mit einem Röntgenpulverspektrum, in dem die Beugungslinien mit maximaler Intensität, die in dem Spektrum des normalen VCl_3 bei $d = 5{,}75 \cdot 10^{-10}$ m, $d = 2{,}67 \cdot 10^{-10}$ m und $d = 1{,}74 \cdot 10^{-10}$ m erscheinen, eine Verbreiterung der Halbpeakbreite um den Faktor von zumindest drei für die Beugungslinie bei $d = 5{,}75 \cdot 10^{-10}$ m und um den Faktor zumindest vier für die bei $d = 2{,}67 \cdot 10^{-10}$ m und $d = 1{,}74 \cdot 10^{-10}$ m erscheinende Beugungslinie aufweisen, oder die Beugungslinien verschwinden,

bei dem eine chlorierte Verbindung des dreiwertigen Vanadins mit einer organischen Verbindung, die zumindest eine OH-Gruppe enthält, umgesetzt wird und das entstandene Reaktionsprodukt bei 30 bis 200°C mit einer halogenierten Substanz, die befähigt ist, mit der in dem Reaktionsprodukt vorhandenen OH-Gruppe zu reagieren, ausgewählt unter den Tetrahalogeniden von Sn oder Si, $Cl_2Si(CH_3)_2$, Cl_3SiCH_3, $SbCl_3$, $AlCl_3$, $TiCl_4$ und $VOCl_3$, zersetzt wird.

2. Verfahren gemäss dem vorhergehenden Anspruch, bei dem VCl_3 als V-Verbindung, C_2H_5OH als organische OH-Gruppen enthaltende Verbindung eingesetzt und die Zersetzung mit $SiCl_4$ durchgeführt wird.

3. Katalysatorkomponente zur Polymerisation von Olefinen, erhalten gemäss dem Verfahren der Ansprüche 1 und 2.

4. Aus einer Komponente gemäss Anspruch 3 gebildete Katalysatorkomponente zur Polymerisation von Olefinen, erhalten durch Zersetzung des Reaktionsprodukts zwischen der chlorierten V-Ausgangsverbindung und der organischen OH-Gruppen enthaltenden Verbindung mit halogenierten Verbindungen, die verschieden sind von halogenierten Ti-Verbindungen, und einer flüssigen halogenierten Ti-Verbindung.

5. Katalysatorkomponente gemäss Anspruch 4, bei der die halogenierte Ti-Verbindung $TiCl_4$ ist.

6. Katalysatorkomponente gemäss den vorhergehenden Ansprüchen, aufgebracht auf $MgCl_2$.

7. Katalysator zur (Co)polymerisation von Olefinen, umfassend das Produkt der Reaktion von

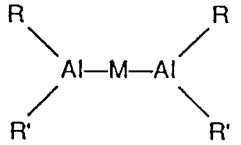
a) einer halogenierten V-Verbindung, erhalten gemäss dem Verfahren der Ansprüche 1 und 2 mit

b) einer metallorganischen Al-Verbindung.

8. Katalysator gemäss Anspruch 7, bei dem in der Formel der Katalysatorkomponente a) $n = 2$, $m = 1$ und R für einen Kohlenwasserstoffrest C_4H_9 steht.

9. Katalysator gemäss Anspruch 7 und 8, bei dem die Komponente a) die Formel $VCl_2(OC_2H_5)$ besitzt.

10. Katalysator gemäss Anspruch 7, bei dem die Komponente b) eine metallorganische Al-Verbindung ist, ausgewählt unter den Al-Trialkylen und Verbindungen der allgemeinen Formel:



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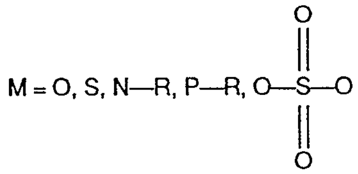


$$M = O,\ S,\ N{-}R,\ P{-}R,\ O{-}\overset{\overset{\textstyle O}{\|}}{\underset{\underset{\textstyle O}{\|}}{S}}{-}O$$

R ein Kohlenwasserstoffrest mit 1 bis 20 C, insbesondere eine Alkylgruppe mit 1 bis 18 C sein kann, R′ R entspricht oder ein Halogen oder ein Alkoxyl ist.

11. Katalysator gemäss den Ansprüchen 7 und 10, worin $M = O$.

12. Katalysator gemäss den vorhergehenden Ansprüchen 7 bis 11, enthaltend das Produkt der Reaktion von

a) $VCl_2(OC_2H_5)$ mit

b) $(iC_4H_9)_2\text{-Al-O-Al-}(iC_4H_9)_2$.

13. Verfahren zur Polymerisation von Ethylen oder zur Copolymerisation von Ethylen mit alpha-Olefinen $CH_2{=}CHR$, worin R für einen Alkylrest mit 1 bis 8 Kohlenstoffatomen steht, zur Herstellung von kristallinen Polymeren und elastischen Copolymeren des Ethylens, dadurch gekennzeichnet, dass die Polymerisation in Gegenwart der Katalysatoren gemäss den Ansprüchen 7 bis 12 durchgeführt wird.

14. Verfahren zur Copolymerisation von Ethylen mit einem alpha-Olefin, ausgewählt unter Propylen, Buten-1, 4-Methylpenten-1, zur Herstellung von elastomeren gesättigten Copolymeren des Ethylens, dadurch gekennzeichnet, dass Monomere in Anwesenheit des Katalysators gemäss den Ansprüchen 7 bis 12 polymerisiert werden.

15. Verfahren gemäss Anspruch 14, dadurch gekennzeichnet, dass die Copolymerisation in Gegenwart eines dritten Monomeren, das mehr als eine Doppelbindung enthält, ausgewählt unter Dienen und Polyenen, durchgeführt wird.

Revendications

1. Un procédé de préparation d'un constituant catalytique pour la polymérisation des oléfines, comprenant un composé chloré de vanadium trivalent présentant la formule générale:

$VCl_n(OR)_m$

dans laquelle:
R est un radical hydrocarbone comprenant 1 à 18 atomes de carbone, notamment un radical alkyle comprenant 1 à 10 atomes de carbone, un radical cycloalkyle comprenant 6 à 8 atomes de carbone ou un radical aryle ou un radical $R^1_pSi(OH)_{3-p}$ dans lequel R^1 est un radical hydrocarboné ayant la même signification que R et $1 \leqslant p \leqslant 3$;
n est un nombre compris entre 1,5 et 3;
m est égal à 3-n;
présentant un spectre de poudre aux rayons X, dans lequel les raies de diffraction d'intensité maximum qui sont obtenues dans le spectre de VCl_3 normal pour $d = 5{,}75 \cdot 10^{-10}$ m, $d = 2{,}67 \cdot 10^{-10}$ m et $d = 1{,}74 \cdot 10^{-10}$ m présentent un élargissement de la moitié de la largeur du pic d'au moins un multiple de trois pour la raie de diffraction à $d = 5{,}75 \cdot 10^{-10}$ m et d'au moins un multiple de quatre pour les raies de diffraction apparaissant à $d = 2{,}67 \cdot 10^{-10}$ m et $d = 1{,}74 \cdot 10^{-10}$ m ou encore ces raies de diffraction disparaissent, procédé dans lequel un composé chlore du vanadium trivalent réagit avec un composé organique, contenant au moins un groupe OH et le produit résultant de la réaction est décomposé entre 30°C et 200°C, par une substance halogénée susceptible de réagir avec le groupe OH présent dans le produit de la réaction, choisie dans le groupe comprenant les tétrahalogénures de Sn ouSi, $Cl_2Si(CH_3)_2$, Cl_3SiCH_3, $SbCl_3$, $AlCl_3$, $TiCl_4$ et $VOCl_3$.

2. Un procédé selon la revendication précédente, dans lequel VCl_3 est utilisé en tant que composé à base de vanadium, C_2H_5OH en tant que compose organique contenant des groupes -OH et la décomposition est effectuée en présence de $SiCl_4$.

3. Constituant catalytique pour la polymérisation des oléfines obtenu selon le procédé des revendications 1 et 2.

4. Constituant catalytique pour la polymérisation des oléfines formées d'un constituant selon la revendication 3, obtenu par décomposition du produit de réaction entre le composé à base de vanadium chloré de départ et le composé organique contenant les groupes -OH avec des composés halogénés différents des composés de titane halogéné, et un composé de titane halogéné liquide.

5. Le constituant catalytique selon la revendication 4, dans lequel le composé de titane halogéné est $TiCl_4$.

6. Le constituant catalytique selon les revendications précédentes, fixé sur un support consistant en $MgCl_2$.

7. Catalyseur pour la (co)polymérisation des oléfines comprenant le produit de la réaction de:

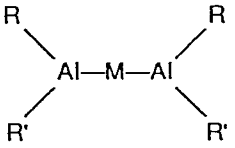
a) un composé halogéné de vanadium obtenu selon le procédé des revendications 1 et 2 avec
b) un composé organo-métallique à base d'aluminium.

8. Un catalyseur selon la revendication 7, dans lequel la formule du constituant catalytique a) n = 2, m = 1 et R est un radical hydrocarboné C_4H_9.

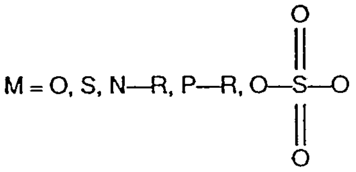
9. Un catalyseur selon les revendications 7 et 8, dans lequel le constituant a) présente la formule:

$VCl_2(OC_2H_5)$

10. Le catalyseur selon la revendication 7, dans lequel le constituant b) est un composé organo-métallique à base d'aluminium choisi parmi les trialkylaluminiums et les constituants présentant la formule générale:



dans laquelle:



$$M = O,\ S,\ N\text{—}R,\ P\text{—}R,\ O\text{—}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}\text{—}O$$

R peut être un radical hydrocarboné comprenant 1 à 20 atomes de carbone et notamment un radical alkyle comprenant 1 à 18 atomes de carbone; et

R′ est égal à R ou est un halogène ou un alkoxyle.

11. Le catalyseur selon les revendications 7 et 10, dans lequel M = O.

12. Le catalyseur selon les revendications 7 à 11 précédentes, comprenant le produit de la réaction de:
a) $VCl_2(OC_2H_5)$ avec
b) $(iC_4H_9)_2\text{-}Al\text{-}O\text{-}Al\text{-}(iC_4H_9)_2$.

13. Un procédé pour la polymérisation d'éthylène ou pour la copolymérisation d'éthylène avec des alpha-oléfines $CH_2{=}CHR$ où R est un radical alkyle comprenant 1 à 8 atomes de carbone, pour préparer des polymères cristallins et copolymères élastiques d'éthylène, caractérisé en ce que la polymérisation est effectuée en présence de catalyseurs selon les revendications 7 à 12.

14. Un procédé pour la copolymérisation d'éthylène avec une alpha-oléfine consistant en propylène, butène-1, 4-méthyl-pentène-1, pour préparer des copolymères élastomères saturés d'éthylène, caractérisé en ce que les monomères sont polymérisés en présence du catalyseur selon les revendications 7 à 12.

15. Un procédé selon la revendication 14, caractérisé en ce que la copolymérisation est effectuée en présence d'un troisième monomère contenant plus d'une double liaison choisi par les diènes et les polyènes.